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(54) Title: METHOD OF IMPROVING THE CRUSHING STRENGTH AND THE IMPACT RESISTANCE OF UREA, AND UREA COMPOSITION

(57) Abstract: The invention relates to a method of improving the crushing strength and impact resistance of urea granules by the addition of an additive comprising a polyvinyl compound of the general formula (CHX-CHY)_n, where n = 4-10 000, and X and Y independently of one another are selected from the group consisting of a hydrogen atom, a hydroxyl radical, carboxylic acid radical, amine radical or amide radical. This method is characterized in that it starts with a urea melt.

Short title: Method of improving the crushing strength and the impact resistance of urea, and urea composition

The invention relates to a method of improving the crushing strength and impact resistance of urea granules by the addition of an additive to the urea, comprising a polyvinyl compound.

5 It is generally known that urea present in the form of prills and granulate urea is subject to crushing during production, storage and transport. Up to 25 wt% of the urea granules may be crushed if the urea granules are moved into a storage tank or storage ship at a relatively high temperature of
10 e.g. more than 40°C.

Even though the urea granules as such do not absorb any moisture and are virtually nonsusceptible to caking, high percentages of crushed granules do lead to dust problems with a strong caking tendency.

15 It is also known that a number of chemical compositions can be used as an additive to improve the crushing strength, the caking tendency and the resistance to moisture.

Formaldehyde, hexamethylenetetramine and formaldehyde/urea condensate products are known as crushing strength improvers, while poly(vinylacetate)/surfactant is used as a moisture resistance improver. All these additives must either be added in relatively large quantities, or the toxic characteristics make them difficult to handle. Moreover, the use of a surface-active component as in poly(vinylacetate)/surface-active agent, results in increased foaming when the urea is used for industrial applications, such as glue, whilst formaldehyde derivatives are unsuitable in the case of melamine production.

There is also a major difference with respect to the use of additives. Formol compounds and the compositions according to the invention are admixed to a urea melt. The polyvinyl/surface-active agent is nevertheless atomized onto a preformed granule.

GB-A-1217106 describes a method of reducing the caking of urea by making use of a poly(vinyl alcohol) having a high

molecular weight as an anticaking additive. More in particular, according to this method, an aqueous solution of the additive is admixed to an aqueous solution of urea. Preferentially, an amount of additive of from 0.005 to 5 wt%, based on the weight 5 of the urea, is admixed.

The concentration of the aqueous urea solution is initially 80%, according to the example given; after admixture of the solution of the additive, concentration up to 95% takes place at elevated temperature, after which the urea is allowed 10 to crystallize by cooling.

The use of PVA as an anticaking additive makes little sense, however, since unstructured urea granules exhibit no caking tendency. Moreover, the large amount of water present and the admixed amount of aqueous PVA cause serious problems in the 15 production process of urea, since all the water has to be evaporated from the urea prior to storage and transport of the granules.

The large amount of water that has to be evaporated again will therefore slow down the production process, i.e. a 20 lesser production results.

An undesirable by-product of urea is biuret which is toxic to plants and animals. The maximum permitted concentration of biuret is 0.75%. Nevertheless, as the residence time of the urea in the production process increases (mainly due to the 25 evaporation of water), the biuret content will be higher.

It is therefore an object of the invention to provide a method by means of which urea having improved crushing strength and impact resistance is obtained and by means of which the abovementioned drawbacks are overcome.

30 The invention therefore relates to a method of the type mentioned in the preamble which is characterized in that a urea melt is admixed with an aqueous solution of a urea additive, comprising a polyvinyl compound of the general formula

35 $(CHX-CHY)_n$,

where n is a number from 4-10 000, and X and Y independently of one another are selected from the group consisting of a hydrogen atom or a polar, organic group, in such a way that the

admixed amount of water is at most 5 wt%, based on the amount of urea, after which the mixture obtained is concentrated to dryness.

The additive is admixed in an amount of at most 5 10 000 ppm, based on the rate of urea, to a melt of urea, with the option of adjusting the melting temperature by the admixture of a small amount of water, after which the melt obtained is concentrated, usually at 100-140°C. This afforded considerable improvements in the crushing strength and impact resistance, in 10 conjunction with the use of relatively small amounts of the additive, said additive as such not being toxic and therefore being readily handled.

As explained hereinabove, the starting point according to the process described in GB-A-1217106 is a solution of urea 15 in water, with a urea concentration of at most 95 wt%; according to the invention, in contrast, the starting point is a urea melt, to which at most 5 wt% of water is admixed.

Preferably, the additive used according to the invention is a polyvinyl compound of the general formula 20 $(CH_2-CHY)_n$, where n is a number from 4 to 10 000, and X and Y independently of one another represent a hydrogen atom or a polar organic group, such as a carboxylic acid radical, ester radical, hydroxyl radical, amine radical, amide radical, more preferably the formula
25 $(CH_2-CHY)_n$, where n = 4-10 000, and Y = a hydrogen atom or a polar organic group, such as a carboxylic acid radical, ester radical, hydroxyl radical, amine radical, amide radical, more preferably the formula
 $(CH_2-CHY)_n$, where n = 4-10 000, and Y = a mixture of an acetate 30 ester radical and hydroxyl group, preferably 70% or more hydroxyl group,
more preferably the formula
 $(CH_2-CHY)_n$, where n = 4-10 000, and Y = a mixture of an acetate ester radical and hydroxyl group, preferably more than 95% 35 hydroxyl group.

An example to be mentioned of a polyvinyl compound having an ester group is a poly(vinyl ester) which can be an acetate ester of an unhydrolysed poly(vinyl alcohol). One example of a polyvinyl compound having a hydroxyl group is a

poly(vinyl alcohol). An example of a polyvinyl compound having an amide group, i.e. a poly(vinylamide), is a polyacrylamide; and an example of a polyvinyl compound having a carboxylic acid group, i.e. a poly(vinylcarboxylic acid), is a poly(maleic acid).

In a preferred embodiment of the invention, the additive chosen is such that the viscosity of a 4% strength solution of the additive in water is between 2 and 100 centipoise, more preferably between 4 and 70 centipoise, at 10 20°C.

Preferably, the additive is employed with the aid of an aqueous solution having a concentration of between 0.5 and 25 wt%, more preferably between 1 and 20 wt%.

Preferably, an aqueous solution of the urea additive 15 having a concentration of from 100 to 10 000 ppm, preferably from 500 to 3 000 ppm, is used.

The invention also relates to a composition comprising a mixture of urea and poly(vinyl alcohol) whose solidification point is from 5 to 15°C, in particular from 10 to 15°C, below 20 the solidification point of urea.

The fact is that applicant has found, surprisingly, that the use of poly(vinyl alcohol) as a urea additive is able to effect a lowering of the solidification temperature of urea. It is precisely this lowering which is very important and as 25 such has never been observed with other additives for urea.

Applicant found, according to a second aspect of the present invention, that the addition of salt(s) to the urea melt, besides the polyvinyl compound, has a favourable effect to the compressibility of the urea granules to be formed, which 30 means that the compressibility of the granules is lowered. This salt (or these salts) can be added separately to the molten urea as an aqueous solution, or together with the aqueous solution of the polyvinyl compound. The amount of water to be added in total may nevertheless not be more than 5 % b.w., based on the amount 35 of urea.

It is observed that the compressibility of granules is a quantity which indicates whether the form of the granules is contained after a certain (storage) period or that there is talk of flattening or other deformation. Urea granules which have a

small compressibility are highly desirable for the use of urea, in an industrial scale, in other processes.

Besides, it is observed that it is known as such from for example US-A-5,676,729 and US-A-5,782,951 to add inorganic 5 material to molten urea to improve the hardness of the urea particles to be formed.

The hardness is nevertheless a quantity, which is measured by applying a large force to the material until fracture takes place.

10 Moreover, according to both abovementioned publications, clays and powders are used. Clays and powders are nevertheless difficult to be handled during the production of urea. Besides, it is due to the bad solubility in the urea melt often impossible to obtain a good dispersion of the additive in the 15 urea.

Preferably, a salt is used according to the invention, whereof the cation is chosen from among the group, consisting of ammonium and the elements from the groups I, II and III of the Periodical System. Preferably, from this group the elements 20 sodium, calcium, magnesium and aluminium are used. Other elements, such as for example potassium or strontium, from these groups can nevertheless also be used.

Expediently, the anion of the salt is selected from the group, consisting of oxide, hydroxide, phosphate, sulphate, 25 nitrate and acetate, preferably sulphate.

According to a preferred embodiment, the total added amount of salt(s) is at most 10 % b.w., based on the total amount of urea.

Further the present application relates to a intimate 30 mixture of urea, a polyvinyl compound and a salt of an inorganic or organic acid, whereby the compressibility of the composition is lower than that of the urea being free of additive.

Preferably the polyvinyl compound is a polyvinylalcohol.

EXAMPLES

35 To demonstrate the effect of the invention, a number of experiments were carried out, employing a method which is representative for production and for testing the quality of the urea granules produced.

PREPARATION METHOD

A urea melt was admixed with an aqueous solution of the additive (of the concentrations specified in the experiments). The urea prills were then formed by allowing molten urea droplets to descend in aliphatic oil having a viscosity of from 5 10 to 50 centipoise at 80°C. After crystallization the prills were taken from the oil and washed with chloroform to remove the oil. The prills can then be screened in order to obtain a particular size. The prills were then dried in a fluidized bed 10 for 1 hour at about 40°C. They were then collected and kept in an airtight flask until the crushing strength and the impact resistance were measured.

MEASURING METHOD

The crushing strength was measured via the IFDC.S-115 15 method.

The impact resistance was measured via the IFDC.S-118 method.

The solidification temperature of the urea samples was measured by the urea melt in question being cooled slowly, but 20 in a controlled manner, in a calorimeter. This was done at a rate of 1°C per minute within the range from 140 to 60°C.

EXPERIMENT 1:

The following additives were tested after the admixture of doses of 3 000 ppm to the urea.

Table 1

Additive	Crushing strength (N)	Impact resistance (% fracture)	Solidification temperature (°C)
Blank	13	75	97
Dynorit S80 (urea/formaldehyde)	15	63	92
HMT (= hexamethylenetetramine)	18	58	91
NH ₄ lignosulphonate	13	72	93
Na lignosulphonate	15	78	95
Ca lignosulphonate	15	75	91
Polyaspartic acid, Na salt	15	62	93
Polyaspartic acid, NH ₄ salt	12	83	92
<u>According to the invention</u>			
2% (w/w) polyacrylamide in H ₂ O	16	60	87
2% (w/w) poly(acrylic acid) in H ₂ O	13	61	87
2% (w/w) poly(maleic acid) in H ₂ O	13	72	87
2% (w/w) poly(vinyl alcohol) in H ₂ O (88% hydrolysed)	17	48	84
2% (w/w) poly(vinyl alcohol) in H ₂ O (98% hydrolysed)	18	29	88

5 Polyvinyl compounds were found to result in an improvement in both the crushing strength and the impact resistance, compared with blank material. Among all the compounds tested, the polyvinyl compounds were found to result in a considerable improvement compared with customary additives such as urea/formaldehyde condensate, HMT and lignosulphonates.

EXPERIMENT 2:

10 The effect of the degree of hydrolysis and the range of the value of n of the polyvinylalcohols were tested in this experiment.

15 3 000 ppm of a 2% (w/w) strength solution of a poly(vinyl alcohol) were admixed to the molten urea prior to prilling.

Table 2

Test	Viscosity Centipoise	Range of value of n	Degree of hydrolysis	Crushing strength (N)	Impact resistance (% fracture)
1	4	~750	88	17	48
2	26	~4 000	88	16	55
3	4	~750	98	18	29
4	28	~4 000	98	21	28

The viscosity was determined of a 4% (w/w) strength solution of the poly(vinyl alcohol) in water at 20°C.

This experiment makes it clear that within a range of n = 4-10 000 a high degree of hydrolysis affords a considerable improvement both in crushing strength and impact resistance.

EXPERIMENT 3:

The effect of the concentration of the active components in the additive.

This experiment made use of the poly(vinyl alcohol) of test No. 3 from Experiment 2. The dose of the additive was 3 000 ppm, based on the weight of the urea.

Table 3

Additive	Crushing strength (N)	Impact resistance (% fracture)
Blank	13	75
2% poly(vinyl alcohol) No. 3 in H ₂ O	18	29
8% poly(vinyl alcohol) No. 3 in H ₂ O	23	6
12% poly(vinyl alcohol) No. 3 in H ₂ O	24	5
16% poly(vinyl alcohol) No. 3 in H ₂ O	20	16

Employing a dose of 3 000 ppm of an 8 to 12% (w/w) strength solution of poly(vinyl alcohol) therefore produces the optimal results in terms of crushing strength and impact resistance.

EXPERIMENT 4:

The effect of the dose of the additive in urea was tested.

The tested solution of the additive consisted of an 8% (w/w) strength solution of the poly(vinyl alcohol) from test No. 3 in Experiment 2.

5 Table 4

Amount of solution ppm	Crushing strength (N)	Impact resistance (% fracture)
Blank	13	75
160	16	57
200	17	61
500	18	36
800	19	25
1 174	19	22
1 560	22	9
1 976	22	5
2 694	21	4
4 000	24	9
5 080	26	12

The optimum dose in urea was therefore found to be between 1 000 and 3 000 ppm, based on the weight of the urea.

EXPERIMENT 5

10 Method of making pellets

An aqueous solution of the additive (having the concentrations indicated in the experiments) was added to an urea melt consisting of 99.7 w/w % urea and 0.3 w/w % water. Thereafter the urea pellets were formed by allowing the molten 15 urea droplets to fall separately from a height of 1 cm onto a glass plate. After solidification the pellets were scraped from the glass plate and the fines where removed by means of a sieve. Then the pellets were collected and kept in an airtight bottle until the compressibility was measured.

20 Method for the determination of the compressibility:

A transparent round tube having an inner diameter of 3 cm was filled with 40 g urea pellets. Onto this a plunger was brought, through which a pressure of about 600 kPa was exerted onto the sample. Directly after the application of the 25 overpressure and again after 24 hours the height of the urea column was measured. The relative difference in height, which is

a measure for the compressibility, was calculated from these two values (Δ height (%)).

Table 5

Additive	Δ height (%)
Blank	16
3000 ppm Dynorit S80 (urea/formaldehyde)	5
2000 ppm of a 8 w/w % polyvinylalcohol nr. 3 in H ₂ O	12
2000 ppm CaSO ₄ .2H ₂ O	8
2000 ppm of a 8 w/w % polyvinylalcohol nr. 3 in H ₂ O having 2000 ppm CaSO ₄ .2H ₂ O	3
2000 ppm MgSO ₄	9
2000 ppm of a 8 w/w % polyvinylalcohol nr. 3 in H ₂ O having 2000 ppm MgSO ₄	3
2000 ppm Na ₂ SO ₄	8
2000 ppm of a 8 w/w % polyvinylalcohol nr. 3 in H ₂ O having therein 2 w/w % Na ₂ SO ₄	5
2000 ppm Ca(OOCCH ₃) ₂	10
2000 ppm of a 8 w/w % polyvinylalcohol nr. 3 in H ₂ O having therein 2 w/w % (Ca(OOCCH ₃) ₂	8
2000 ppm of a 8 w/w % polyvinylalcohol nr. 3 in H ₂ O having therein 2 w/w % Ca(H ₂ PO ₄) ₂	13
2000 ppm of a 8 w/w % polyvinylalcohol nr. 3 in H ₂ O having therein 2 w/w % (NH ₄) ₂ SO ₄	10
2000 ppm of a 8 w/w % polyvinylalcohol nr. 3 in H ₂ O having therein 2 w/w % Al ₂ (SO ₄) ₃	9

5

From the results mentioned in table 5 the favourable effect of the addition of a salt to the compressibility of the urea granulate appears clearly.

CLAIMS

1. A method of improving the crushing strength and impact resistance of urea granules by the addition of an additive to the urea, consisting of a polyvinyl compound, characterized in that to a urea melt, an aqueous solution of a urea additive, consisting of a polyvinyl compound of the general formula $(CHX-CHY)_n$, where $n = 4-10\ 000$, and X and Y independently of one another are selected from the group consisting of a hydrogen atom or a polar, organic group, is added in such a way that the added amount of water is at most 5 wt%, based on the amount of urea, after which the mixture obtained is concentrated to dryness.
- 15 2. A method according to claim 1, characterized in that an additive is used of the formula specified in claim 1, wherein the said polar organic group is selected from a carboxylic acid group, an ester group, a hydroxyl group, an amine group and an amide group.
- 20 3. A method according to claim 1 or 2, characterized in that a urea additive is added as described in claim 1 or 2, wherein X is a hydrogen atom and Y substantially consists of a hydroxyl group.
- 25 4. A method according to one or more of claims 1 to 3, characterized in that at least 70%, preferably at least 95%, of Y consists of a hydroxyl group.
- 30 5. A method according to one or more of claims 1 to 4, characterized in that an additive is used, whereof the viscosity of a 4% strength solution of the additive in water is between 2 and 100 centipoise at 20°C.
- 35 6. A method according to claim 5, characterized in that an additive is used whereof the viscosity of a 4% strength solution of the additive in water is between 4 and 70 centipoise at 20°C.
7. A method according to one or more of claims 1 to 6, characterized in that an aqueous solution of the urea additive having a concentration of from 0.5 to 25 wt% is used.
8. A method according to one or more of claims 1 to 7, characterized in that an aqueous solution of the urea additive having a concentration of from 1 to 20 wt% is used.

9. A method according to one or more of claims 1 to 8, characterized in that an aqueous solution of the urea additive having a concentration of from 100 to 10 000 ppm, preferably from 500 to 3 000 ppm, is used.
- 5 10. A composition consisting of an intimate mixture of urea and poly(vinyl alcohol) whose solidification point is from 5 to 15°C, in particular from 10 to 15°C, below the solidification point of the urea.
11. A composition according to claim 10, the composition 10 containing at most 3 000 ppm of poly(vinyl alcohol), based on the weight of the urea.
12. A method according to one or more of the claims 1 to 9, characterized in that further a salt of an inorganic or organic acid is added to the urea melt, such that the total added amount 15 of water is at most 5 wt%, based on the amount of urea.
13. A method according to claim 12, characterized in that a salt is used whereof the cation is selected from the group, consisting of ammonium, and the elements from the groups I, II and III of the Periodical System, preferably the elements 20 sodium, calcium, magnesium and aluminium from these groups.
14. A method according to claim 12 or 13, characterized in that a salt is used, whereof the anion is selected from the group, consisting of oxide, hydroxide, phosphate, sulphate, nitrate and acetate, preferably sulphate.
- 25 15. A method according to one or more of the claims 12 to 14, characterized in that the amount of salt(s) to be added in total is at most 10 wt%, based on the amount of urea.
16. A composition consisting of an intimate mixture of urea, a polyvinyl compound and a salt of an inorganic or organic 30 acid, the compressibility of the composition being lower than that of the urea being free of additive.
17. A composition according to claim 16, characterized in that the polyvinyl compound is polyvinylalcohol.